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**Oxygen Plasma Resistant  
Phosphine Oxide Containing  
Imide/Arylene Ether Copolymers**

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RESISTANT PHOSPHINE OXIDE  
CONTAINING IMIDE/ARYLENE COPOLYMERS  
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# OXYGEN PLASMA RESISTANT PHOSPHINE OXIDE CONTAINING IMIDE/ARYLENE ETHER COPOLYMERS

by

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## INTRODUCTION

As part of an effort to develop high performance structural resins for aerospace applications, work has continued on block copolymers containing imide and arylene ether segments. The copolymers reported herein represent an extension of previous work<sup>1-5</sup> on these materials. The arylene ether block used in this study contains a phosphine oxide unit in the polymer backbone while the imide block is a known crystalline imide with excellent properties named LaRC<sup>TM</sup>-CPI<sup>6</sup> for Langley Research Center Crystalline Polyimide.

A few copolymers containing an imide block and some other blocks have been reported. Most notably, the copolymers containing imide and siloxane blocks have received considerable attention<sup>7-10</sup> and more recently, polyimide-polyformal block copolymers<sup>11</sup>, triblock copolymers containing imide-aryl ether phenylquinoxaline blocks<sup>12</sup> and imide-aryl ether ketone block copolymers<sup>13</sup> have been reported. The preparation of amine-terminated sulfones by a method similar to that used herein has been reported.<sup>14</sup> The incorporation of phosphorus into polymers is known to improve fire resistance<sup>15</sup> and atomic oxygen resistance.<sup>16</sup> Recently poly(arylene ethers) containing phenyl phosphine oxide (PPO) were shown to exhibit good weight retention after exposure to simulated atomic oxygen.<sup>17,18</sup>

## EXPERIMENTAL

**Monomers** - Bis(4-fluorophenyl)phenyl phosphine oxide (FPPO), (m.p. 123 °C) was prepared following a known procedure.<sup>19</sup> 2,2-Bis(4-hydroxyphenyl)hexafluoropropane (6AF) was obtained commercially and recrystallized twice from toluene to yield a white solid (m.p. 160-161 °C). 1,3-Bis(4-aminophenoxy-4'-benzoyl)benzene (BABB) (m.p. 161.5-164 °C) was obtained from DayChem Laboratories, Inc. 3,3',4,4'-Benzophenonetetracarboxylic dianhydride (BTDA) was obtained commercially and vacuum sublimed to yield a white crystalline solid (m.p. 224-226 °C). 4- Aminophenol was obtained commercially and vacuum sublimed to yield a white crystalline solid (m.p. 185-187 °C).

**Oligomers** - The amine-terminated poly(arylene ethers) (ATAE) were synthesized as shown in Eq. 1 by aromatic nucleophilic substitution of FPPO with 6AF and 4-aminophenol in N,N-dimethylacetamide (DMAc) using potassium carbonate. The oligomers were prepared at two different calculated molecular weights ( $\bar{M}_n$ ) by adjusting the monomer ratio (6AF/DFBP) to 0.7825 and 0.8582 to provide  $\bar{M}_n$ s of 2500 and 4000 g/mole, respectively. The anhydride-terminated polyamide acids (ATAA) were prepared in DMAc as shown in Eq. 2 by adjusting the monomer ratio (BABB/BTDA) to 0.821 and 0.906 to provide calculated  $\bar{M}_n$ s of 4000 and 8000 g/mole, respectively.

**Copolymers** - The copolymers were prepared by adding a solution of the ATAE in DMAc to the ATAA solution and stirring overnight under nitrogen. For example, to prepare ATAE 2500/ATAA 4000 block copolymer, BTDA (0.8056 g, 2.500 mmol) was added to a solution of BABB (1.0273 g, 2.0524 mmol) and DMAc (10.4 g). The mixture was stirred for 6 h to form a clear solution. A solution of ATPAE 2500 (1.1456 g,

0.4582 mmol) in DMAc (6.5 g) was added to the polyamide acid solution prepared above to form a clear, viscous solution which was stirred overnight. These block copolymers were then cast as a film on plate glass and dried 1 h each at 100, 200 and 300 °C to form a tough, creasible cyclodehydrated copolyimide film, ATAE 2500/ATI 4000. Alternatively, the copolymers were solution imidized by adding toluene to the reaction mixture and heating to 155 °C overnight to collect a toluene/water azeotropic mixture, providing an insoluble powder.

Characterization - Inherent viscosities ( $\eta_{inh}$ ) were obtained on 0.5% solutions in chloroform (CHCl<sub>3</sub>) at 25 °C for FPPO/6AF and in DMAc at 25 °C for the other polymers and copolymers. Differential scanning calorimetry (DSC) was performed at a heating rate of 20 °C/min with the apparent  $T_g$  taken at the inflection point of the  $\Delta T$  versus temperature curve.

Films - DMAc solutions (15% solids) of the polymers were centrifuged, the decantate doctored onto plate glass and dried at room temperature to a tack-free form in a low humidity chamber. The films on glass were dried 1 h each at 100, 200 and 300 °C. Mechanical tests were performed as recommended in ASTM D882 on at least four specimens per test condition.

Oxygen Plasma Asher Exposure- Simulated atomic oxygen exposures were preformed on thin films (0.5 in x 0.5 in, ~2 mils thick) in a Tegal Plasmod Asher. The Asher was operated at 500 millitorr, 100 Watts of radio frequency, O<sub>2</sub> pressure of 3 psi and a flow rate of 50 cm<sup>3</sup>/min. Since the Asher was not calibrated, simultaneous exposures of Kapton® were preformed. Exposures were preformed for up to 15 h and the weight loss of the films monitored as a function of exposure time.

## RESULTS AND DISCUSSION

ATAEs with calculated  $\bar{M}_n$ s of 2500 and 4000 g/mole were prepared by offsetting monomer stoichiometry. These oligomers had  $\eta_{inh}$ s of 0.082 and 0.124 dL/g and  $T_g$ s of 173 and 186 °C, respectively. When the oligomers were reacted with a stoichiometric amount of BTDA, the  $\eta_{inh}$ s increased to 0.95 and 0.87 dL/g and the  $T_g$ s increased to 218 and 216 °C for the ATAЕ 2500/BTDA and ATAЕ 4000/BTDA, respectively. The high  $\eta_{inh}$ s obtained indicated that the calculated  $\bar{M}_n$ s were essentially correct. The FPPO/6AF was prepared with an  $\eta_{inh}$  of 0.86 dL/g and a  $T_g$  of 213 °C while LaRC™-CPI has a  $T_g$  of 222 °C and a  $T_m$  of 350 °C.

Four different block copolymers were prepared as shown in Table I from the ATAЕ and ATAA oligomers. The copolymers were prepared by reacting a stoichiometric ratio of oligomers (using calculated  $\bar{M}_n$ s) producing polyamide acids with  $\eta_{inh}$ s ranging from 0.42 to 0.80 dL/g in DMAc. The cured copolyimide films were characterized by DSC and results are shown in Table 1.  $T_g$ s range from 224 to 228 °C, slightly higher than the  $T_g$ s of either homopolymer. The ATAЕ 2500/ATI 8000 also displayed a small endotherm in the DSC curve at 335 °C indicating the presence of some crystallinity.

Tensile properties of the clear yellow-orange films of the copolymers and homopolymers are shown in Table 2. The polyimide has higher strength and modulus than the arylene ether as expected. The tensile strength and modulus of the copolymers varied widely with tensile strength as high as 16.1 ksi and tensile modulus as high as 439 ksi. Each of the films displayed properties intermediate to those of FBB/BPF and LaRC™-CPI homopolymers.

Results from the oxygen plasma exposure are shown in Fig. 1 which plots weight loss of the films versus time of exposure. Each of the phosphine oxide containing copolymers displays higher weight retention than the Kapton® for the same

exposure times and films with higher concentration of phosphine oxide display better weight retention than films with lower concentrations.

## CONCLUSIONS

A series of imide/arylene ether block copolymers were prepared containing phosphine oxide. These copolymers displayed a relatively high modulus and high resistance to oxygen plasma etching, a combination of properties needed for matrix materials for certain applications of composites in space.

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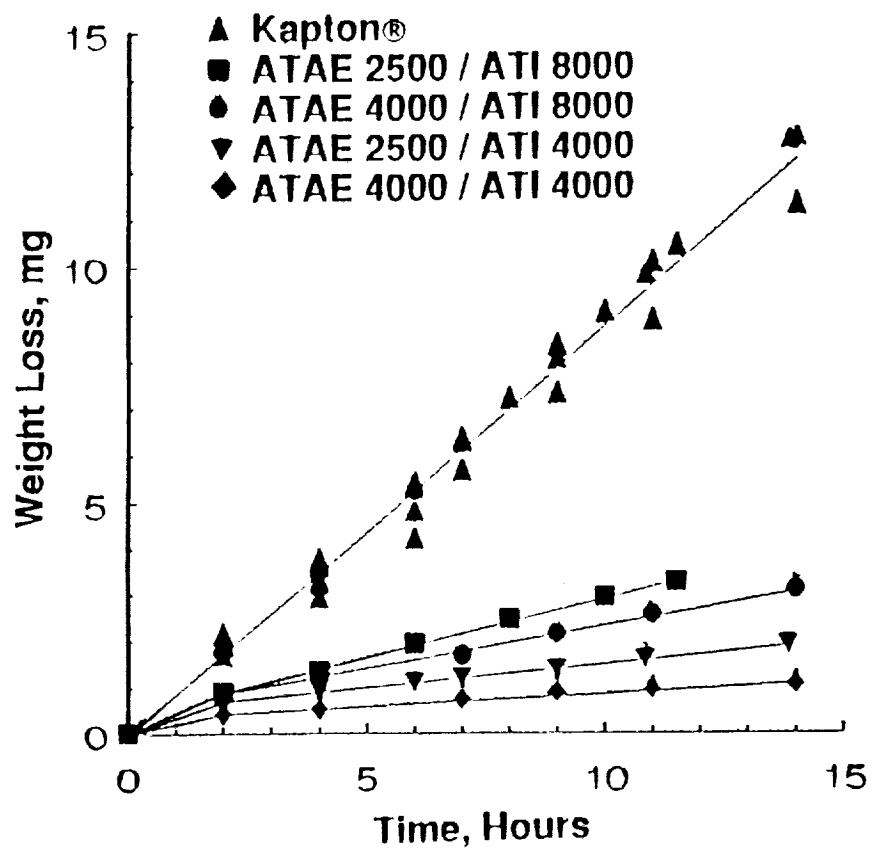
TABLE 1. CHARACTERIZATION OF COPOLYMERS

Copolymer	$\eta_{inh}$ , dL/g, (Polyamic acid)	T <sub>g</sub> , °C, by DSC
ATAE 2500/ATI 4000	0.80	228
ATAE 2500/ATI 8000	0.42	228
ATAE 4000/ATI 4000	0.42	224
ATAE 4000/ATI 8000	0.58	225

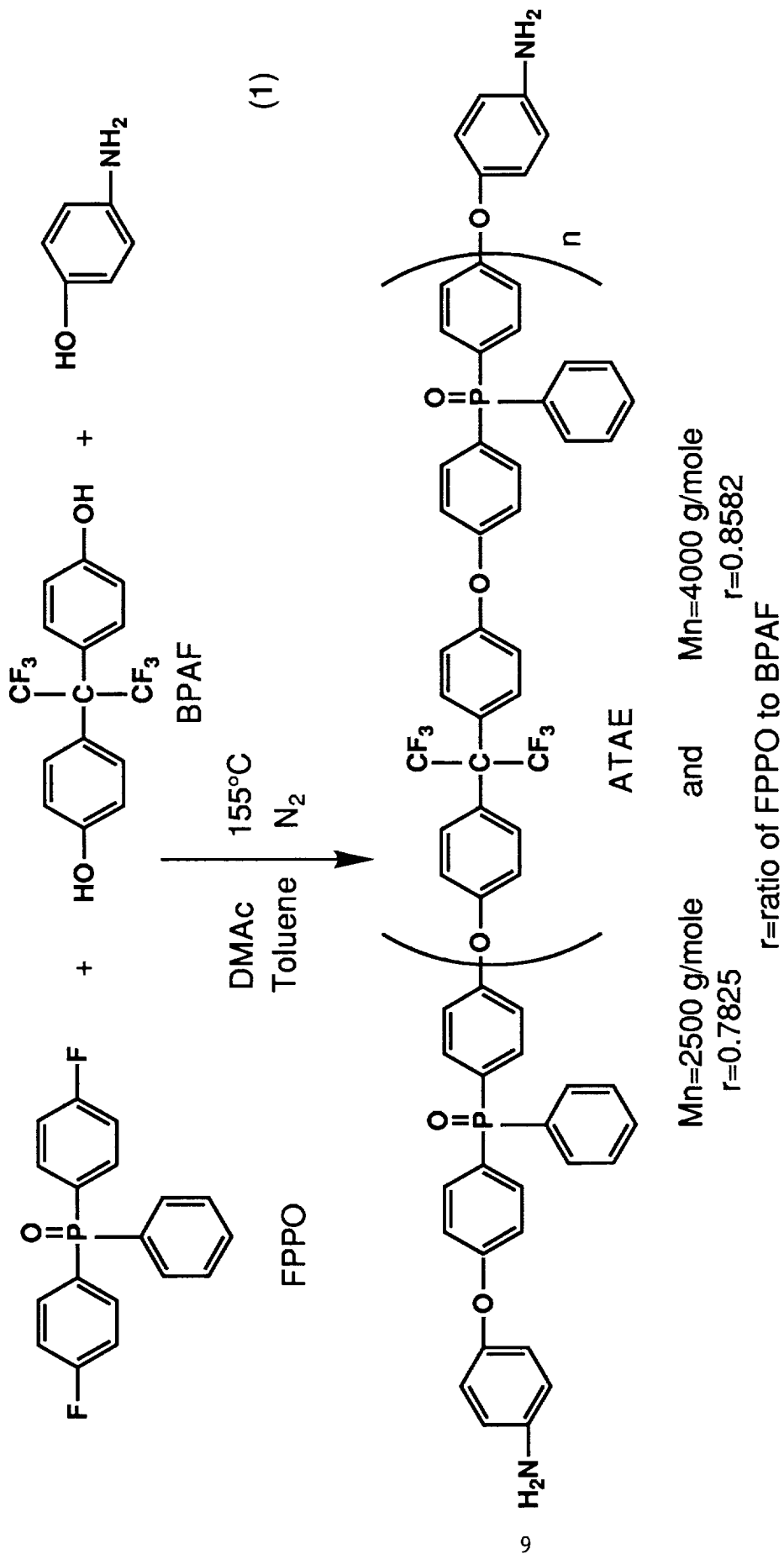
TABLE 2. THIN FILM PROPERTIES OF POLYMERS AND COPOLYMERS.

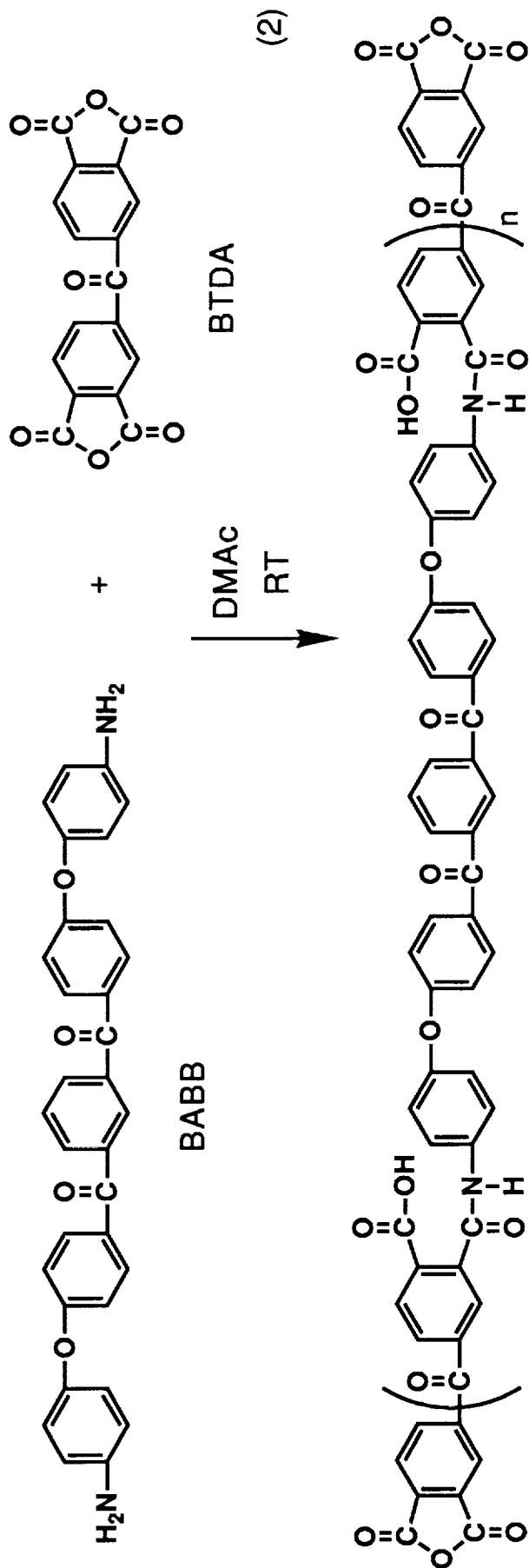
POLYMER	TENSILE STRENGTH, KSI (TENSILE MODULUS, KSI) [ELONGATION, %]	
	RT	150°C
ATAE 2500/ ATI 4000	14.7 (375) [23]	8.8 (287) [43]
ATAE 2500/ ATI 8000	16.1 (439) [8.5]	9.1 (299) [22]
ATAE 4000/ ATI 4000	10.8 (379) [3.7]	6.4 (308) [2.5]
ATAE 4000/ ATI 8000	15 (412) [11.1]	8.0 (250) [97]
Imide Homopolymer	22.0 (630) [8.3]	15.2 (540) [21] <sup>1</sup>
Arylene Ether Homopolymer	9.9 (280) [36]	6.4 (260) [80]

<sup>1</sup>Tested at 177°C.



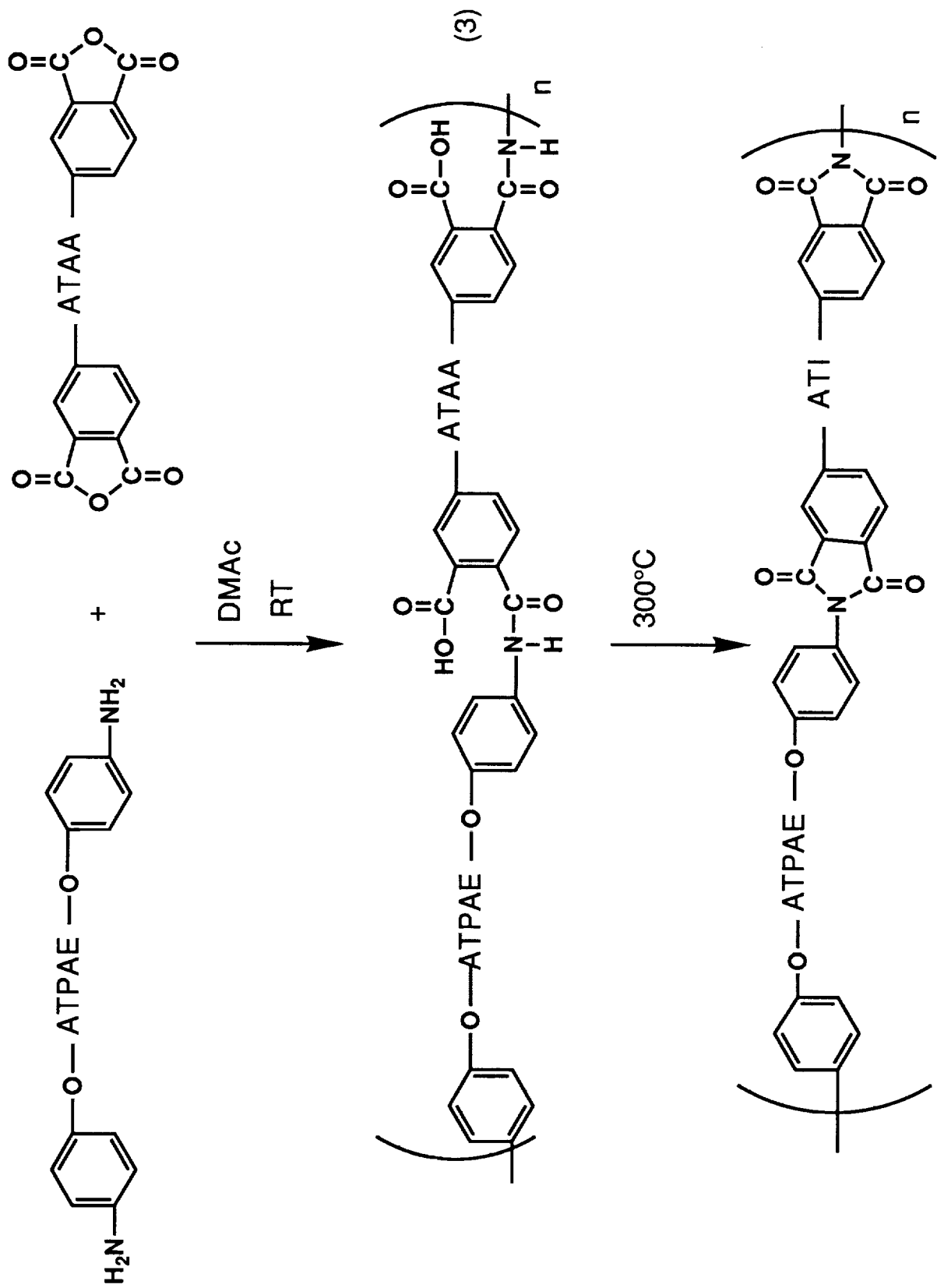
**Figure 1. Oxygen Plasma Etching of Phosphine Oxide Containing Copolymers.**





ATAA  
(ATI, imidized)

Mn=4000g/mole and Mn=8000g/mole  
 r=0.821 and r=0.906  
 r= ratio of BABB to BTDA



IMIDE/ ARYLENE ETHER BLOCK COPOLYMERS

# REPORT DOCUMENTATION PAGE

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